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EXECUTIVE SUMMARY

FOURIER TRANSFORM INFRARED SPECTROSCOPY - AN INTRODUCTION

O. Herrmann

Analytical Services Section
Chemical Research Department

The Chemical Research Department has acquired a Fourier transform infrared (FTIR) spectrometer to replace a dispersive infrared spectrometer in the Analytical Services Section. The new instrument offers many new capabilities in both data acquisition and manipulation.

The basic principles of FTIR spectroscopy are discussed with emphasis on the reasons why it offers much greater sensitivity than a dispersive instrument. A summary of the currently available hardware is provided to help plan future experiments.

The main body of the report describes the application of the basic system and the various accessories to different sampling situations. A brief outline is given for each technique and examples are provided of the types of spectra which can be obtained. These include the spectra of thin films, bulk polyvinyl chloride, powdered resin and gases.

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To: Mr. F.J. Kee
Director of Research

FOURIER TRANSFORM INFRARED SPECTROSCOPY - AN INTRODUCTION

O. Herrmann

A brief introduction to Fourier transform infrared spectroscopy (FTIR) is provided. Three surface analytical techniques (specular reflectance, attenuated total reflectance and diffuse reflectance) are discussed and a number of examples are provided which demonstrate the application of each technique. Although FTIR spectroscopy allows the study of formerly impossible samples, sample preparation remains a critical stage in the analysis. Operator judgment and spectral interpretation are more important than ever before.

1.0 BACKGROUND

Infrared capabilities were established at Ontario Hydro over twenty years ago under the direction of S. Takahashi. At this time, infrared spectroscopy was relatively novel in industrial applications and Ontario Hydro exploited it for material identification and specification verification. Unfortunately, the instrumentation was not updated over the years and infrared spectroscopy gradually fell into disuse as it failed to resolve new more demanding problems.

Although many improvements were made over the years, a quantum leap occurred with the development and commercialization of Fourier transform infrared (FTIR) spectrometers. These instruments were able to deal with many formerly intractable samples using new techniques which required much greater sensitivity than was possible with conventional dispersive instruments. In addition, since the new instruments were inherently computer based, many spectral manipulations could be routinely implemented which could be achieved with older instrumentation only with difficulty. With time the price of FTIR instruments has decreased to the point where the price of a good dispersive instrument is currently about equal to that of a medium grade FTIR instrument which has much greater capabilities. The price/performance ratio favors Fourier transform

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infrared spectrometers over dispersive instruments in so many applications that Fourier transform instruments are gradually replacing dispersive models. In fact, Beckman instruments, a major supplier of infrared spectrometers has discontinued the manufacture of dispersive instruments.

Another new development has been the tunable diode laser instrument. This instrument can provide unparalleled resolution and finds application in the analysis of atmospheric pollutants. The major drawback of tunable diode lasers, however, is the limited spectral range.

In 1985, the Chemical Research Department acquired a Mattson Cygnus 25 FTIR spectrometer, a mid-level instrument with surface analysis capabilities. Further accessories can be added to the instrument as required, thereby extending its capabilities to meet new needs.

This report describes some of the capabilities of the instrument based on our initial experience. It will require some time to fully utilize instrumental capabilities because of the great change relative to the former dispersive instrument.

2.0 GENERAL PRINCIPLES

A dispersive instrument consists of 3 main component assemblies:
(1) a source of infrared radiation;
(2) a monochromator, which disperses the radiant energy into its many frequencies, together with a series of slits or apertures which selects the narrow band of frequencies to be examined;
(3) a detector which converts the energy of the narrow band of frequencies into an electrical signal which can be amplified and recorded in some way.

In comparison, the Fourier transform instrument design is similar in having source and detector assemblies but has an interferometer in place of the monochromator/aperture set. The most commonly used interferometer is the Michelson interferometer (Figure 1). Here the radiation (not dispersed) strikes a beam-splitter so that half of the radiation is transmitted and half is reflected. Both beams pass on to mirrors then are reflected back to the beam-splitter where they are recombined. Half of this radiation travels back toward the source while the other half continues on to the sample area. From this derives one of the advantages of FTIR spectroscopy, the throughput advantage (called Jacquinot's advantage). Half of the radiation passes on to the sample whereas in a dispersive instrument only a narrow band of wavelengths, a very small portion of the total beam, reaches the sample.

One of the mirrors described above is fixed while the other one is

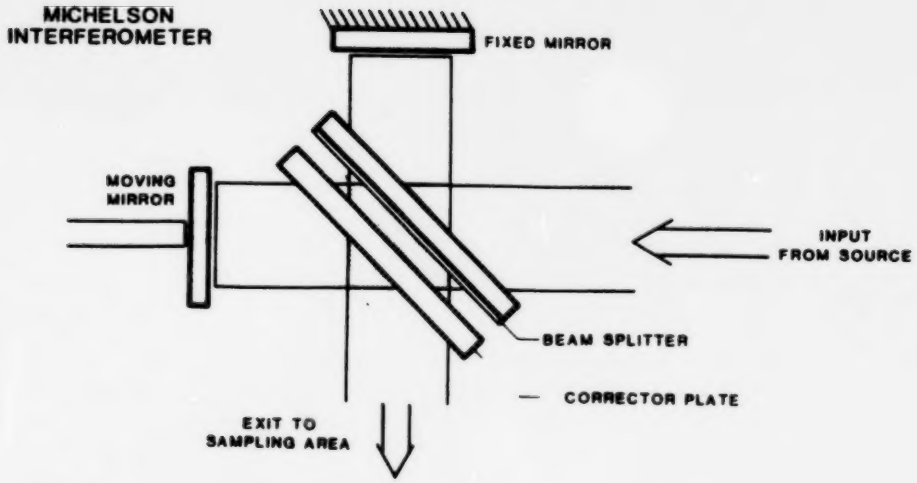

FIGURE 1

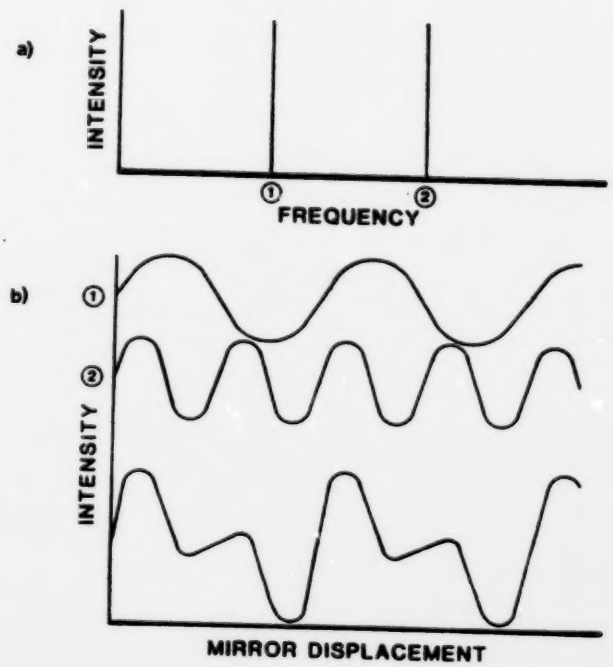

FIGURE 2

mobile. When the two mirrors are at equal distances from the beam-splitter and monochromatic radiation is used, then radiation at the exit beam will be essentially unchanged except for being reduced to one half of the original intensity. If the movable mirror is now moved 1/4 of the wavelength of the radiation, an optical retardation (increase in optical pathlength) of 1/2 of a wavelength is produced along that path since the radiation must travel to and from the mirror. When this beam is recombined with the beam which went to the fixed mirror, destructive interference will occur (the radiation beams cancel each other) and no radiation output is observed. Thus as the mirror is moved there will be successive regions of constructive and destructive interference - the radiation output will increase and decrease alternately as a function of the distance that the mirror is moved (Figure 2), forming a cosine wave. When radiation of a different wavelength is used, the mirror displacements at which constructive and destructive interferences occur will be different. Thus when a broad band radiation source (contains many different wavelengths) is used, a complex pattern of intensities is obtained as a function of mirror displacement which is a superposition of the patterns obtained for each wavelength (as shown in Figure 2). This complex pattern, which consists of overlapping cosine waves, is called the interferogram. A portion of an interferogram is shown in Figure 3. Only at the point where the mirrors are at equal distances from the beam-splitter is there constructive interference of all wavelengths. This is the point of greatest intensity in the interferogram and is called the centerburst. The fact that every point in the interferogram contains information about every wavelength present results in greater efficiency in gathering information during a scan than results using a dispersive instrument where information is collected about each wavelength in turn only once during each scan. This is referred to as the multiplex advantage or Felgett's advantage. The process of converting an interferogram into familiar spectral format can be viewed as resolving the cosine waves and determining the intensity of each cosine at every frequency. This conversion process is accomplished by means of a mathemathical algorithm known as the Fourier transform. A more rapid algorithm called the fast Fourier transform (fft) was developed by Cooley and Tukey in 1965 /1/ and it was first applied to spectroscopy in 1966 /2/. This algorithm, in combination with reasonably priced minicomputers, made FTIR practical. Further developments in computers have resulted in the production of microcomputer based systems as well (at a greatly reduced price).

A third advantage is the precision of wavelength measurement (Connes' advantage). The position of the moving mirror can be clocked using a helium-neon laser passing through the interferometer. The interference fringes from the laser beam are used to trigger the data collection points along the mirror's travel.

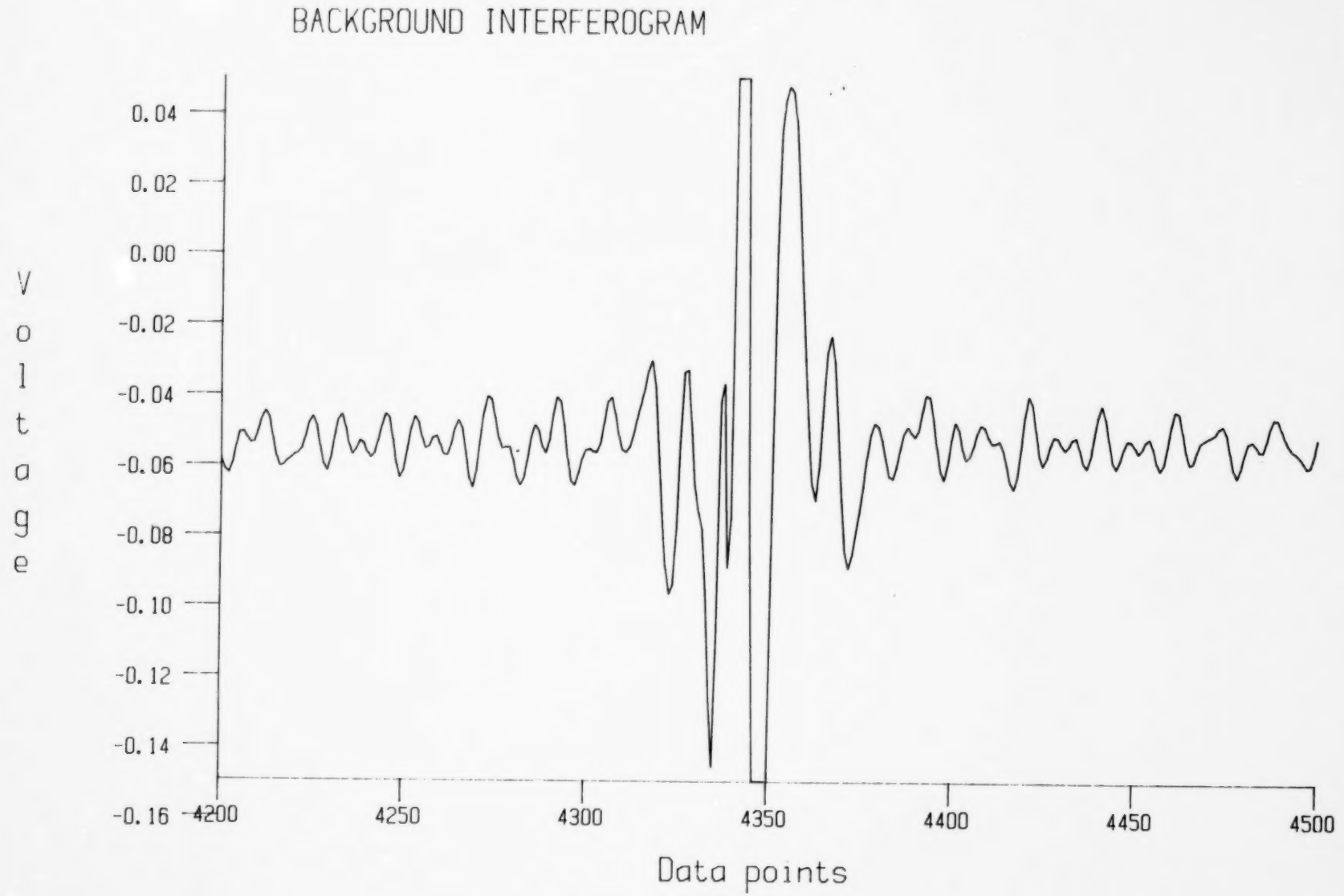

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FIGURE 3

Since the frequency of the laser is known, the frequencies in the interferogram can be precisely calculated. Because the mirror movement is precisely clocked, the interferogram can be collected and averaged many times to improve the signal to noise ratio (S/N). The S/N increases as the square root of the number of scans (eg. increasing the number of scans by a factor of 9 improves S/N by a factor of 3). The precision of the wavelength measurement is, in fact, essential for the operation of the FTIR spectrometer. Most FTIR instruments are single-beam in contrast to dispersive instruments which are double-beam. Figure 4 shows a single-beam spectrum of an empty nitrogen-purged sample compartment. The energy detected can be seen to vary widely across the spectral range with the maximum occurring around 1200 cm-1. The various features are due to gases in the radiation path and the materials of construction (the features around 3700 and 1700 cm-1 are due to water vapour; those at 2350 are due to residual carbon dioxide; other small features arise from the coating on the beam-splitter). This spectrum is ratioed with the single-beam spectrum of the sample to obtain a background - corrected spectrum. Thus it is important to get a point-by-point correspondence on the frequency (or wavelength) scale to obtain a true sample spectrum. In a double-beam instrument, such a ratio would be automatically obtained by the hardware. Figures 5A and 5B show a typical 100 % line obtained by ratioing two successive runs (16 scans each) of the background and the same line on an enlarged scale. Note that as the energy decreases at the two ends of the spectrum (Figure 4), the noise increases. In addition, good wavelength precision is important (especially long term precision) for spectral subtraction, an important utility.

There are many important aspects to implementing Fourier transform spectroscopy both in hardware and software. The general principles are discussed in reference texts /3, 4, 5/. Griffith's well known book /3/ is the best all-round text to date although a new edition is expected. Specific aspects and developments in FTIR spectroscopy are discussed in journals such as American Laboratory (mostly manufacturer-based information), Analytical Chemistry and Applied Spectroscopy. Applied Spectroscopy currently carries the most relevant articles and a perusal of back issues can provide a good perspective of the direction of developments.

3.0 INSTRUMENT DESCRIPTION

This section describes the current configuration of the system. Some of the description will not be generally useful but can serve as a reference for those interested in the details of the FTIR spectroscopic hardware itself or for planning future experiments. A summary of the major specifications is given in Table 1.

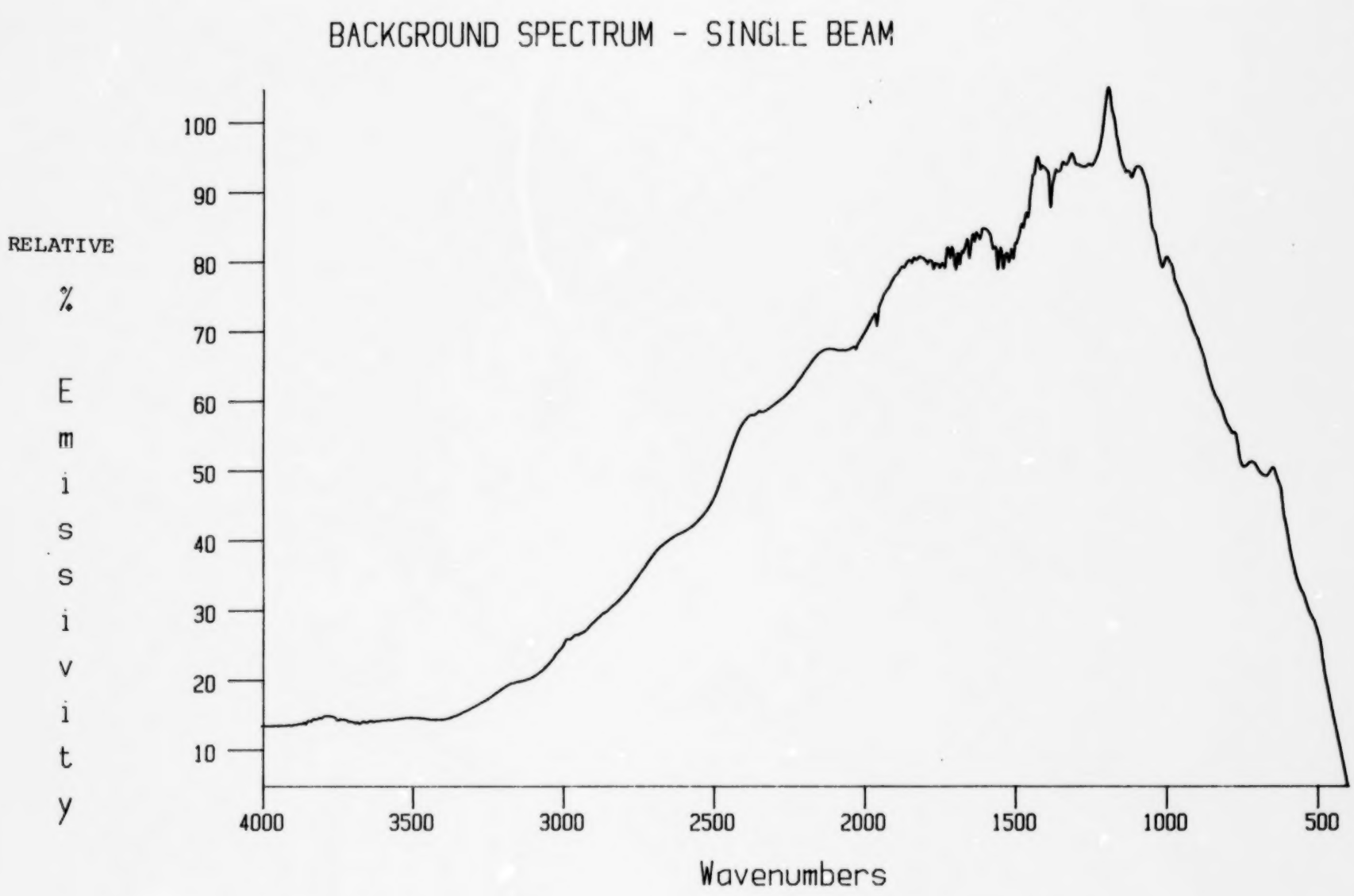

FIGURE 4

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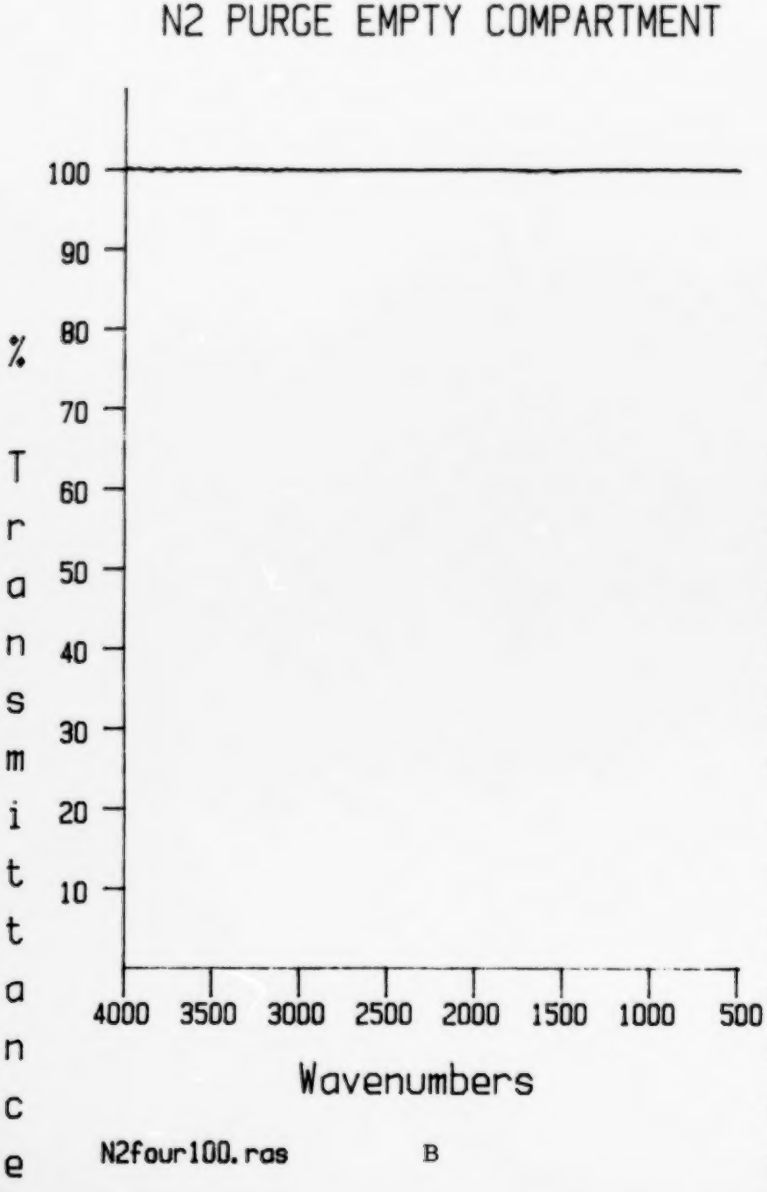
N2 PURGE EMPTY COMPARTMENT
% Transmittance
100
90
80
70
60
50
40
30
20
10
4000 3500 3000 2500 2000 1500 1000 500
Wavenumbers
N2four100.ras
B

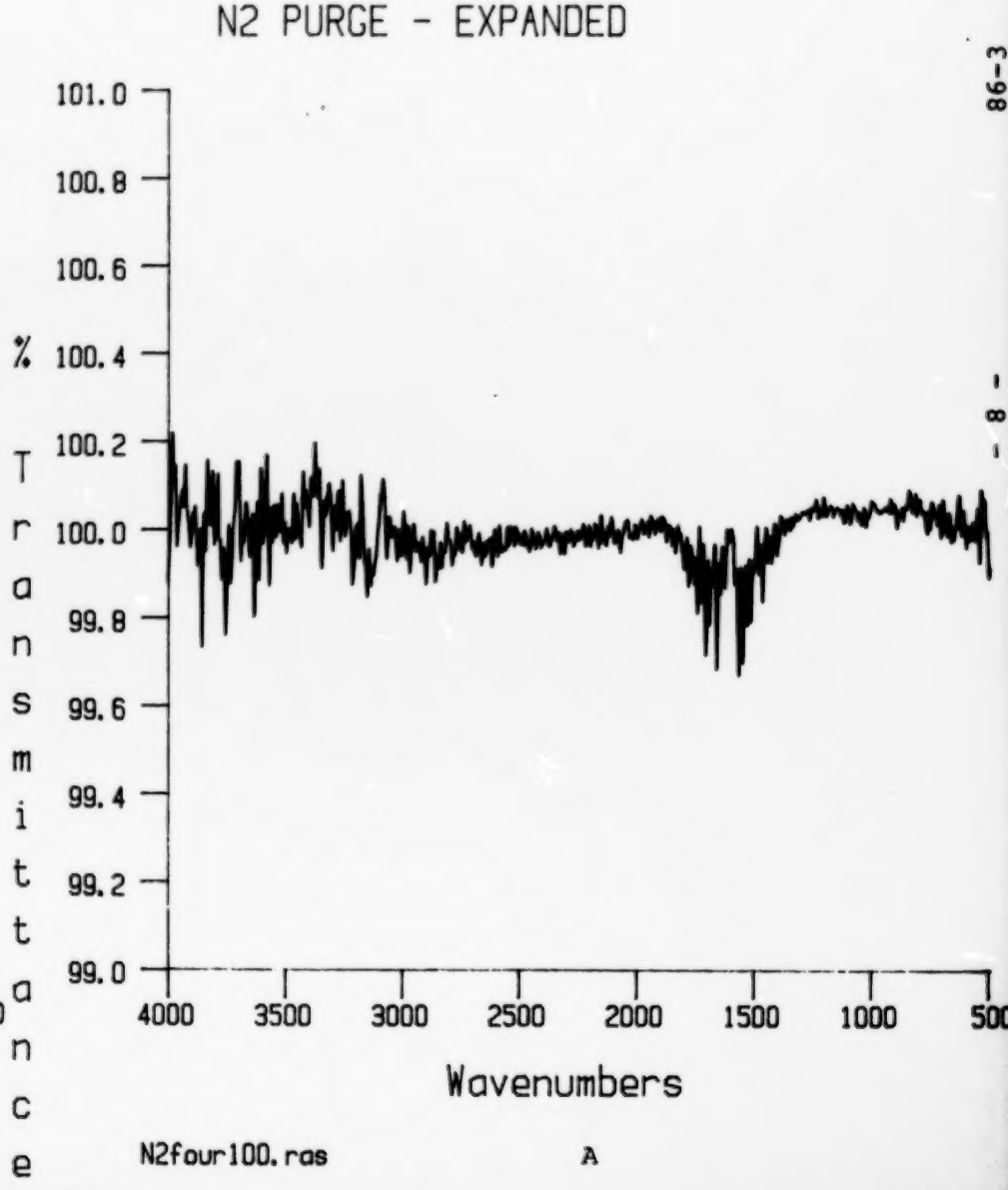
N2 PURGE - EXPANDED
% Transmittance
101.0
100.8
100.6
100.4
100.2
100.0
99.8
99.6
99.4
99.2
99.0
4000 3500 3000 2500 2000 1500 1000 500
Wavenumbers
N2four100.ras
A

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FIGURE 5

TABLE I
SUMMARY OF SPECIFICATIONS

SPECTROMETER	
Source	air-cooled resistance-heated wire
Beam-splitter	KBr with proprietary coating
Interferometer mirrors	corner cube; the fixed mirror is adjustable by micrometer screws
Detector	deuterated triglycine sulfate
Wavelength reference	He-Ne laser
Analog/digital converter	25 kHz; 15 bit with sample and hold
Sample compartment	50 cm wide x 28 cm deep x 20 cm high
Normal transmission	simple sample holder and two F/3 mirrors
Universal Sampling stage	has 3 micrometer screw adjusted mirrors for reproducible positioning. Used for micro transmittance, ATR, and specular reflectance. An F/1 mirror and a flat mirror (neither one on the stage itself) are used in conjunction with this sampling stage instead of the F/3 mirrors.
Micro transmission	holder adjustable in X and Y directions
ATR holder	different crystals can be used; can be set to 30, 45 and 60 degrees angle of incidence
Specular reflectance holder	Simple non-adjustable sample stage
Diffuse reflectance	Fixed configuration stage with its own mirrors used with an F/3 mirror off-stage
DATA PROCESSING AND DISPLAY HARDWARE	
I/O processing	TI9900 processor with 128 kB RAM
Spectrometer interface	Motorola 68000 procesor with 128 kB RAM
Central processor	Motorola 68000 processor with 1 MB RAM
Data storage	40 MB Winchester disk
Archival storage	600 kB floppy disk (8 inch)
User interface	Visual 550 monochrome (green, 14 inch screen) terminal with 768x585 pixel graphics display and 80 character x 34 lines text display. The keyboard has normal typewriter alphanumeric keys, cursor control keys, numeric keypad and 12 programmable keys.
Plotter	Hewlett-Packard 7470A 2-pen plotter

3.1 General Features

The Cygnus 25 has an air-cooled resistance-heated wire source and a coated KBr beam-splitter. This limits the operating range of the instrument to 5000 to 400 cm-1 (the mid infrared), although it is generally used in the range 4000 to 500 cm-1. The S/N decreases rapidly outside the generally used range, especially at < 500 cm-1 because of a combination of reduced radiation output from the source and decreasing efficiency of the optics (primarily the beam-splitter). The S/N could be improved within this range (needed for diffuse reflectance with certain samples for example) by changing to a water-cooled source with an iris (a much more intense source: the iris regulates throughput to match requirements). Further improvement could be obtained within the mid infrared by changing the current deuterated triglycine sulfate (DTGS) detector to a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector although the wavelength range is more restricted than with a DTGS detector. A different beam-splitter and source are required to change the operating range to either near or far infrared.

A helium-neon laser wavelength reference is used together with polarized interferometer positioning (to signal the start of data collection). An analog filter network is used with detector preamplification and a 25 kHz 15 bit analog to digital converter with sample and hold. I/O is handled by a Texas Instruments 9900 processor with 128 kB of memory. The system has a high speed interface for signal averaging and to handle communication between the spectrometer and the system computer. The interface is run by a Motorola 68000 processor with 128 kB of dual port random access memory (RAM). The dual port RAM allows direct memory access by either the spectrometer or the system computer, thereby increasing performance.

Available optical resolutions are 0.5, 1, 2, 4, 8, 16 and 32 cm-1. Generally, 4cm-1 resolution is used for working with solids and liquids and 0.5 cm-1 for gases. Lower resolution is used in each case when faster data acquisition is required.

The system computer which handles all data storage and manipulation is a Pixel 100 microcomputer which also uses a Motorola 68000 processor with 1 MB of RAM, a 40 MB Winchester disk as the main storage device and an 8 inch floppy (about 600 kB formatted capacity) as a backup. The operating system and spectral manipulation software occupy about 20 MB of the hard disk. There is also a small (about 2000 spectra) Sadtler library of polymer pyrolysates plus library search software which occupy about 10 MB, leaving about 10 MB for daily use. Spectra use up disk space fairly rapidly so that the user area must be erased regularly (the frequency at which this is done varies drastically depending on how heavily the

instrument is used). Data which may be required in the future are stored on floppy disks while everything else is simply erased. There is no programming language on the system at present (although these are available) but simple programs can be built up based on existing spectral manipulation commands and operating system (a subset of Unix) commands. These can be very useful to simplify repetitive tasks.

General interaction with the system including spectral manipulation is accomplished via a Visual 550 monochrome terminal. This is a low resolution graphics terminal with a graphics display format of 768x585 pixels and a text display of 34 lines of 80 characters/line. The capabilities of the terminal are generally underutilized by the existing software.

Spectra are plotted on a Hewlett-Packard 7470A plotter (2 pen). A wide range of formats can be used including scaling, overlays, offsets and X-axis linear in microns or cm-1.

3.2 Current Sampling Accessories

A. Holder for normal transmission studies

The holder is a simple non-adjustable type which accommodates KBr pellets or plates, standard liquid cells and gas cells up to 10 cm in length.

B. Universal sampling stage

This sampling stage holds three mirrors whose position can be changed with micrometer screws. The stage provides a five-fold beam condensation and is used with three accessories:
(i) Micro transmission holder - This is the same type of holder as used with regular transmission except that the sample stage itself can be adjusted in the X-Y plane with micrometer screws. This accessory is useful for small samples or inclusions within larger samples (areas not of interest are masked). The micro transmission holder cannot be used with gas cells because the holder is very close to a mirror.
(ii) Attenuated total reflection (ATR) stage - A number of crystals with different refractive indexes can be used with incident angles of 30, 45 and 60 degrees. The infrared beam is passed along the length of the crystal by multiple internal reflections and interacts with samples in contact with the crystal. This accessory is used for pliable solids, powders or liquids. The sample must make good contact with the crystal.
(iii) Specular reflection stage - The particular stage in use is a fixed angle type only. It is used for smooth shiny solids or films on solid substrates.

C. Diffuse reflection stage

The diffuse reflectance stage contains its own set of fixed mirrors and is used with powders and dull, scattering surfaces. This particular stage cannot be adapted to different sample sizes and thus solid samples must be cut to fit the holder which is 6 mm in diameter and 3 mm deep.

3.3 Available Accessories for Expansion

This section provides a summary of some available accessories with approximate prices. This may be of help in planning experiments which are currently beyond the instrument's capabilities.

3.3.1 Interface to Gas Chromatograph

The ability to interface a gas chromatograph to the infrared spectrometer is extremely useful in the analysis of complex organic samples. The infrared spectrum of mixtures is generally too complex for interpretation and prior separation of the components is required. Gas chromatography is widely used for separations and its addition greatly increases the utility of the infrared spectrometer. GC-FTIR is generally regarded as complementary to gas-chromatography / mass spectrometry (GC-MS). In order to implement GC-FTIR, the following are required:
(1) a more sensitive detector - a mercury-cadmium telluride (MCT) liquid nitrogen cooled detector
(2) a faster analog-to-digital converter (16 bit, 40 kHz)
(3) heated transfer line and light pipe
(4) software
Total cost of implementation would be about $40,000 if the GC itself is available. Detection limits of about a nanogram can be achieved. However, in order to approach the detection limits of a GC-MS system, a cryogenic matrix isolation system (sample components are trapped in solid argon) would be required which costs about $200,000.

3.3.2 Photoacoustic Spectroscopy Attachment

This attachment is used for highly irregular and highly absorbing samples (eg. lump of coal, carbon black). Photoacoustic spectroscopy is used for applications which are similar to diffuse reflectance but for samples which do not provide acceptable spectra with it. The method is, however, difficult to use in practice, and is thus not widely used. Approximate cost of implementation would be $20,000.

3.3.3 Microscopic Attachment

The microscopic attachment is used for the examination of inclusions in larger samples or for very small samples. Cost is $20,000.

3.3.4 Extension of Wavelength Range

The wavelength range can be extended into either the near or far infrared by means of a new source, detector and beam-splitter. Extension in either direction costs about $16,000.

3.3.5 Attenuated Total Reflectance for Liquids

ATR is very useful for solutions in highly absorbing solvents but the sample holder used is different from that used for solids. The cost varies from $1000 to $6000 depending mostly on the total pathlength (determined by crystal shape and size).

3.3.5 Mercury-Cadmium Telluride Detector

This type of detector greatly increases the sensitivity in the mid-infrared region. It is useful for all techniques but is essential for GC-IR, kinetic studies and for many samples using diffuse reflectance. Approximate cost $17,000 - $20,000.

3.3.6 Water-cooled Source and Iris

A more intense source improves S/N in all techniques. The iris is required to optimize intensity and beam size for specific set-ups. This combination is required for use with the MCT detector. Cost is about $5000.

3.3.6 Spectral Library and Additional Winchester Storage

At present, the system has a small spectral library of polymer pyrolysates. A spectral library is a great aid in identification although it is not unambiguous. However, spectral libraries require considerable storage space, thus additional spectra would need extra storage capacity. A collection of 10,000 spectra with the required storage would cost about $40,000.

3.3.7 Variable-Angle Specular Reflectance Accessory

The use of a variable-angle attachment allows the determination of film thickness and index of refraction. Conditions for obtaining the spectra of thin films and multiple-layered thin films can be optimized. The current attachment is a fixed-angle unit. Cost is about $1000.

3.3.8 Specular Reflectance Accessory for Large Samples

This attachment is useful for large samples which cannot be cut to size readily or which must be examined non-destructively. One application is the examination of lubricants on the surface of floppy disks. The accessory is a fixed-angle type and costs about $3000. A stepper motor can be added for automated surface mapping for about $5000.

3.3.9 Vacuum Chamber for Diffuse Reflectance

This attachment allows examination of samples in controlled atmospheres and elevated temperatures. However, this attachment requires a diffuse reflectance accessory which can accommodate large samples. The chamber costs about $5000. The diffuse reflectance accessory itself would cost about the same.

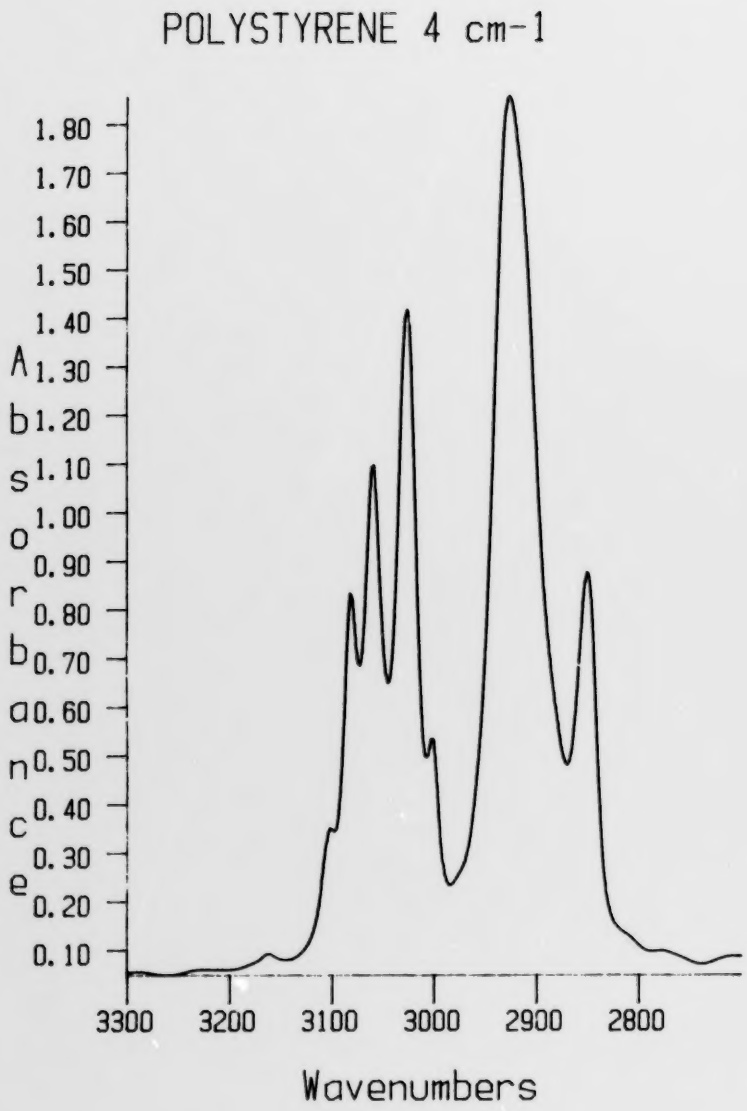
The above accessories represent some of the additional capabilities which are available for the FTIR spectrometer. There are many other accessories available to meet special requirements.

4.0 APPLICATIONS

A number of applications are described below to demonstrate instrument capabilities. These are meant to be illustrative rather than comprehensive.

4.1 Normal Transmission Mode

Figures 6A and 6B show a portion of a spectrum of a 0.05 mm thick polystyrene film obtained using different resolutions. These spectra illustrate the flexibility of plotting. Although the entire spectrum from 5000 to 400 cm-1 was obtained in each case, only a selected portion is shown with automatic scaling along the Y-axis. Any portion of the spectrum can be recalled and displayed or plotted at will. In this case, the plots are scaled along the X-axis to allow two spectra per page. Scaling can be arbitrarily changed along either one or along both axes. These figures also demonstrate an important fundamental point - until the resolution becomes significantly better than the inherent linewidth of a peak, increasing the resolution results in increased absorbance of the peak. Obviously, narrow peaks will be much more sensitive to changes in resolution than broad peaks. Thus the relative peak heights and the spectral appearance can be affected by the resolution used. Unfortunately, increased resolution means increased time for data acquisition, thus a reasonable compromise must be worked out. In most cases, 4 cm-1 resolution is adequate for qualitative work with solids and solutions although lower resolution may have to be used when fast data acquisition is required, as


POLYSTYRENE 4 cm-1
Absorbance
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
3300
3200
3100
3000
2900
2800
Wavenumbers
ref4.abs
A

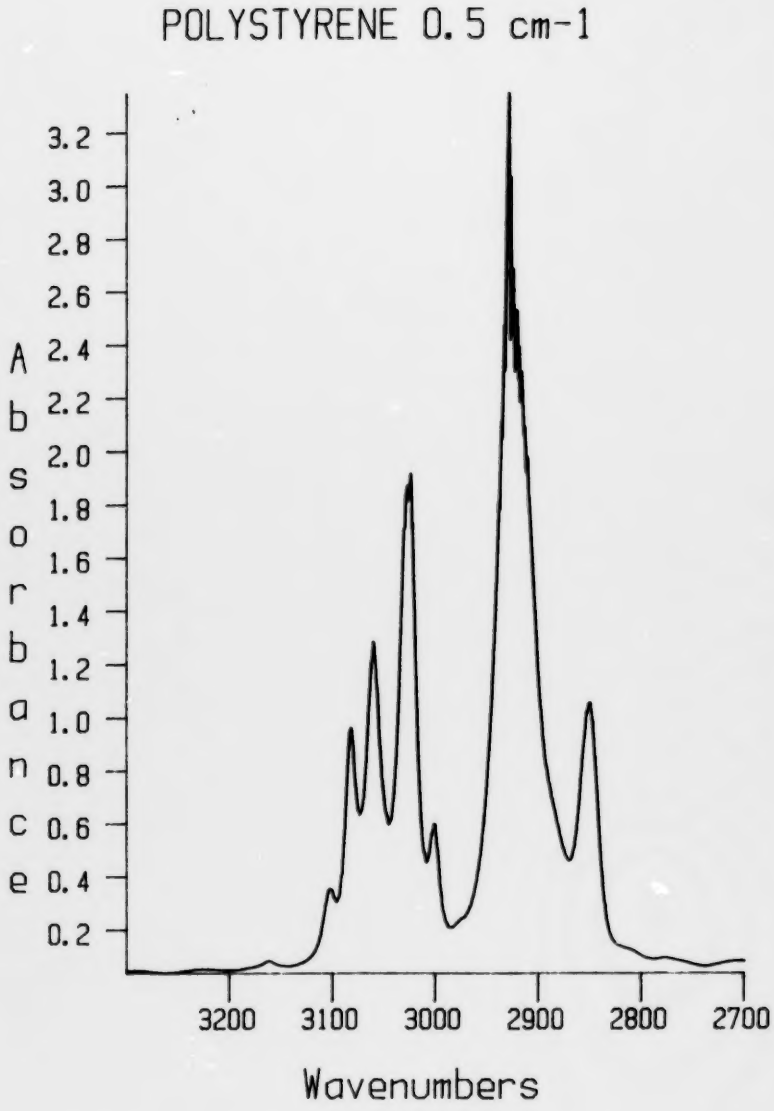

POLYSTYRENE 0.5 cm-1
Absorbance
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
3200
3100
3000
2900
2800
2700
Wavenumbers
refhalf.abs
B

FIGURE 6

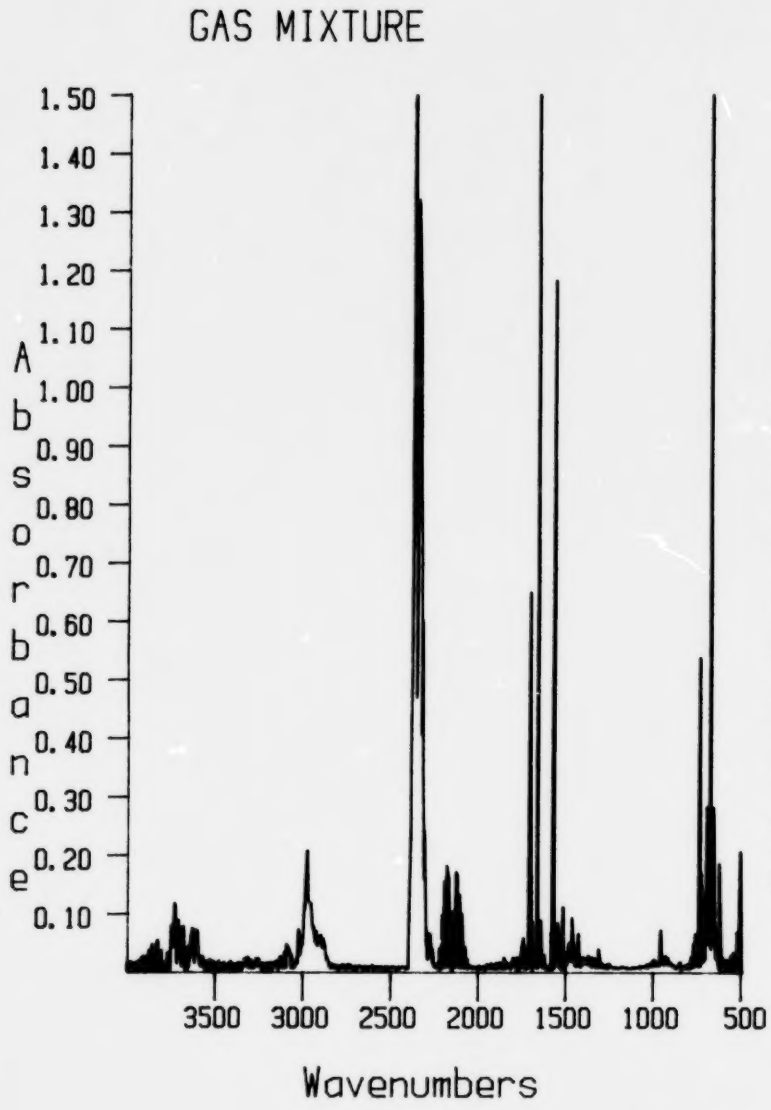
in GC-FTIR or studies of reaction kinetics. Figures 6A and 6B show that the qualitative appearance of the spectra is not severely affected by improving the resolution from 4 to 0.5 cm-1 for a solid but the actual absorbance values can be significantly changed. Thus in 6A, the maximum absorbance is about 1.85 while it is 3.25 in 6B. Because calibrants are used, either resolution will be acceptable for quantitative work, but improving the resolution will improve both the sensitivity and the linearity of the calibration. Whether the actual detection limit (using the same number of sample scans) is also improved will depend on how much the noise is increased relative to the apparent absorbance at the frequency of interest (as mentioned above, there is a greater absorbance increase for narrow peaks). The noise increases in proportion to the increased resolution. Thus improving the resolution by a factor of two decreases the S/N by a factor of square root of two. Therefore, the S/N can be brought back to the original level by increasing the number of scans by two. However, since the time to do each scan at the higher resolution is also doubled, the total spectral acquisition time is quadrupled in order to achieve the same S/N as at the lower resolution. The increase in time required becomes significant when low S/N already requires a large number of scans and a relatively large improvement in resolution is desirable.

Figure 7A is the high resolution (0.5 cm-1) spectrum of a gas mixture showing the rotational fine structure of various components. The portion corresponding to carbon monoxide is shown in Figure 7B. Comparison with Figure 6B shows that the line widths in the gas mixture are much narrower (as expected) and that one should use as high a resolution as possible.

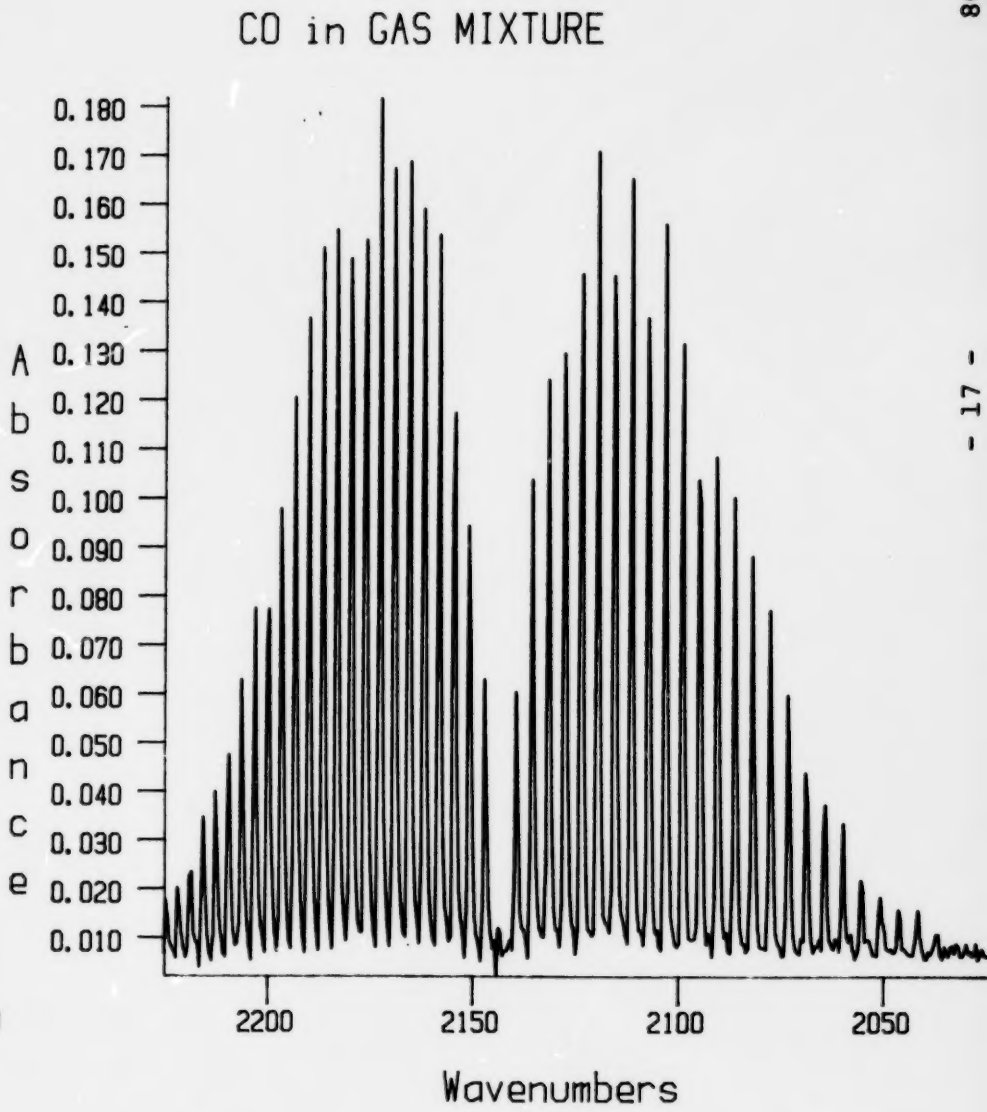
4.2 Specular Reflectance Spectroscopy

Specular reflectance involves direct reflection of the IR beam from the sample surface - a mode that most people are used to with conventional light and reflecting surfaces. Some of the radiation interacts with the sample surface before being reflected. The technique is most often used with thin layers of absorbing material on a reflecting substrate (generally a metal surface). By varying the angle of incidence it is possible to examine different thicknesses of material. Monolayer sensitivities can be achieved using grazing angles and a polarized beam. Specular reflection from the surface of a bulk material can only be used under special circumstances and is of little use because the resulting spectra are quite different from the normal transmission spectra. The Analytical Services Section has a fixed angle attachment only for general use.

A piece of aluminum foil was cleaned with Freon (1,1,2- trichloro-1,2,2-trifluoroethane) and air-dried. A background spectrum was



gasaug15.abs A



gasaug15.abs B

FIGURE 7

obtained using this sample. A fingerprint was placed on the foil and the spectrum obtained is shown in Figure 8 (100 scans). Besides showing the sensitivity of the method, this demonstrates that care is required in handling samples, otherwise one can end up trying to identify the fingerprint instead of the sample.

A real application of this method was exemplified by a piece of aluminum plate with a number of dark areas which was submitted from Bruce NGS. Although the spots could be described as black, the coating was thin enough to be transparent (the metal underneath was clearly visible). A "clean" area was used as the reference (background spectrum) and compared with a dark spot. The resulting spectrum (Figure 9; 50 scans) is essentially that of water (broad peaks around 3400, 2100 and 1600 cm-1). The peak at 1060 cm-1 may indicate some sulfate. No change was observed after heating the sample for several hours at 110° C. This indicated that the bands were due to very strongly adsorbed water or water of hydration. Energy dispersive X-ray fluorescence failed to show significant amounts of any other elements. Thus, in spite of the black colour, the stains appeared to be hydrated aluminum oxide.

4.3 Attenuated Total Reflectance

In attenuated total reflectance (ATR), the infrared beam is passed through a crystal of higher refractive index than the sample. In the Cygnus 25, a parallelogram shaped crystal is used, although other shapes can be used depending on the optical path of the particular instrument and ATR attachment. The angle of incidence of the IR beam is greater than the critical angle and thus total internal reflection occurs. The beam passes down the length of the crystal by multiple reflections off the crystal faces and exits at the far end of the crystal through the face which is parallel to that through which it entered. The sample is kept in contact with one or both of the reflecting faces. At each point of reflection the IR beam does, in fact, penetrate slightly into the sample. The penetrating portion is called the evanescent wave and can be either absorbed by the sample or reflected back into the crystal. Thus the beam is affected by sample absorption similarly to transmission and a spectrum is obtained. The need for good contact between the crystal and the sample represents one of the major limitations of the technique. Bulk solid samples must be moderately flexible at least for good contact and powders should be as fine as possible to maximize the contact area. A point of concern is the hardness of the sample relative to the crystal - harder materials will damage the crystal face, severely degrading performance. Liquids present no problem as long as they can be held in contact with the crystal and do not dissolve it. Special ATR attachments are generally used for liquids to prevent sample loss by flow and evaporation. The small depth of penetration of the beam is a particular advantage

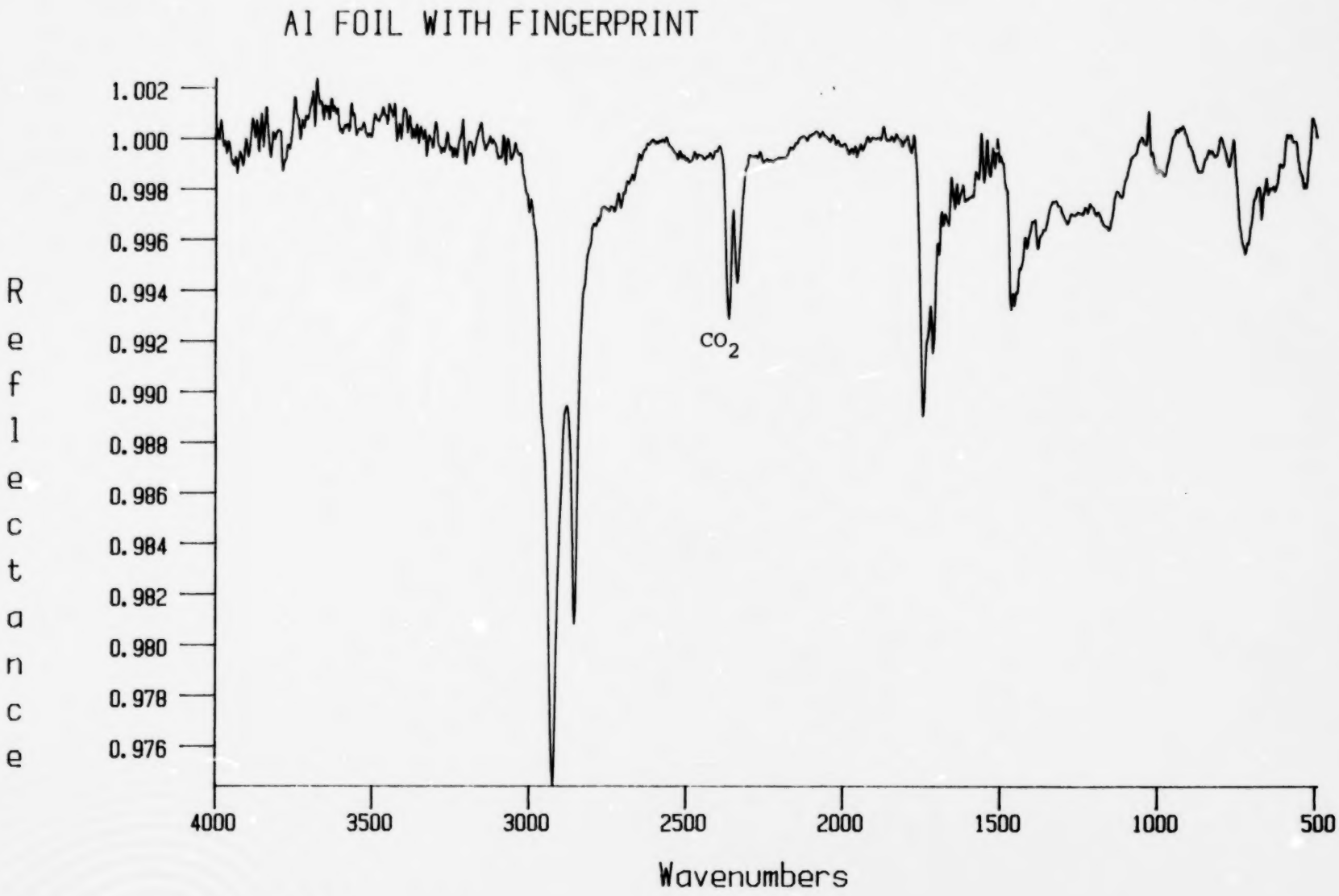
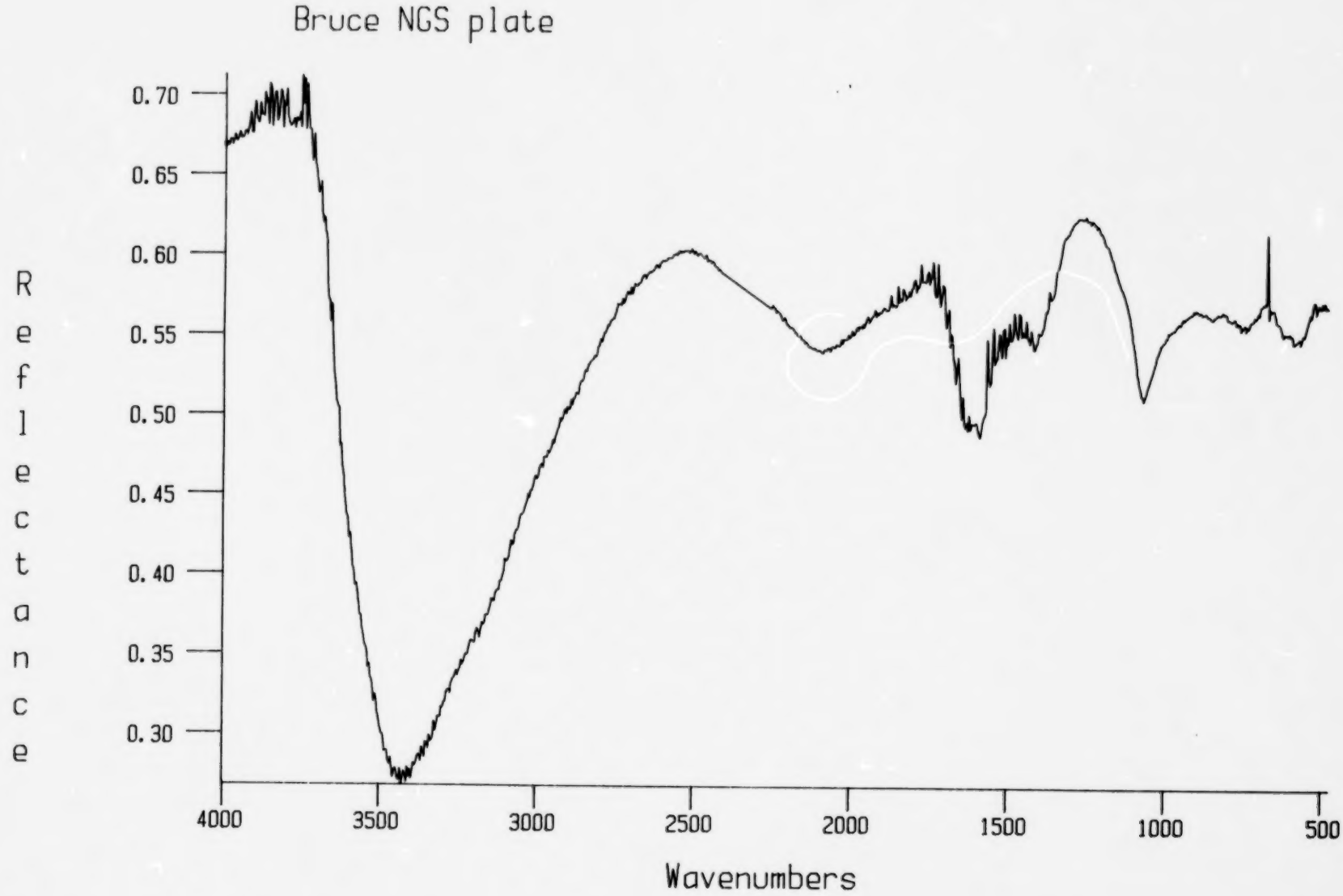

Al FOIL WITH FINGERPRINT
Reflectance
1.002
1.000
0.998
0.996
0.994
0.992
0.990
0.988
0.986
0.984
0.982
0.980
0.978
0.976
CO_2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
al2.ras

FIGURE 8



specwbkgln.ras

FIGURE 9

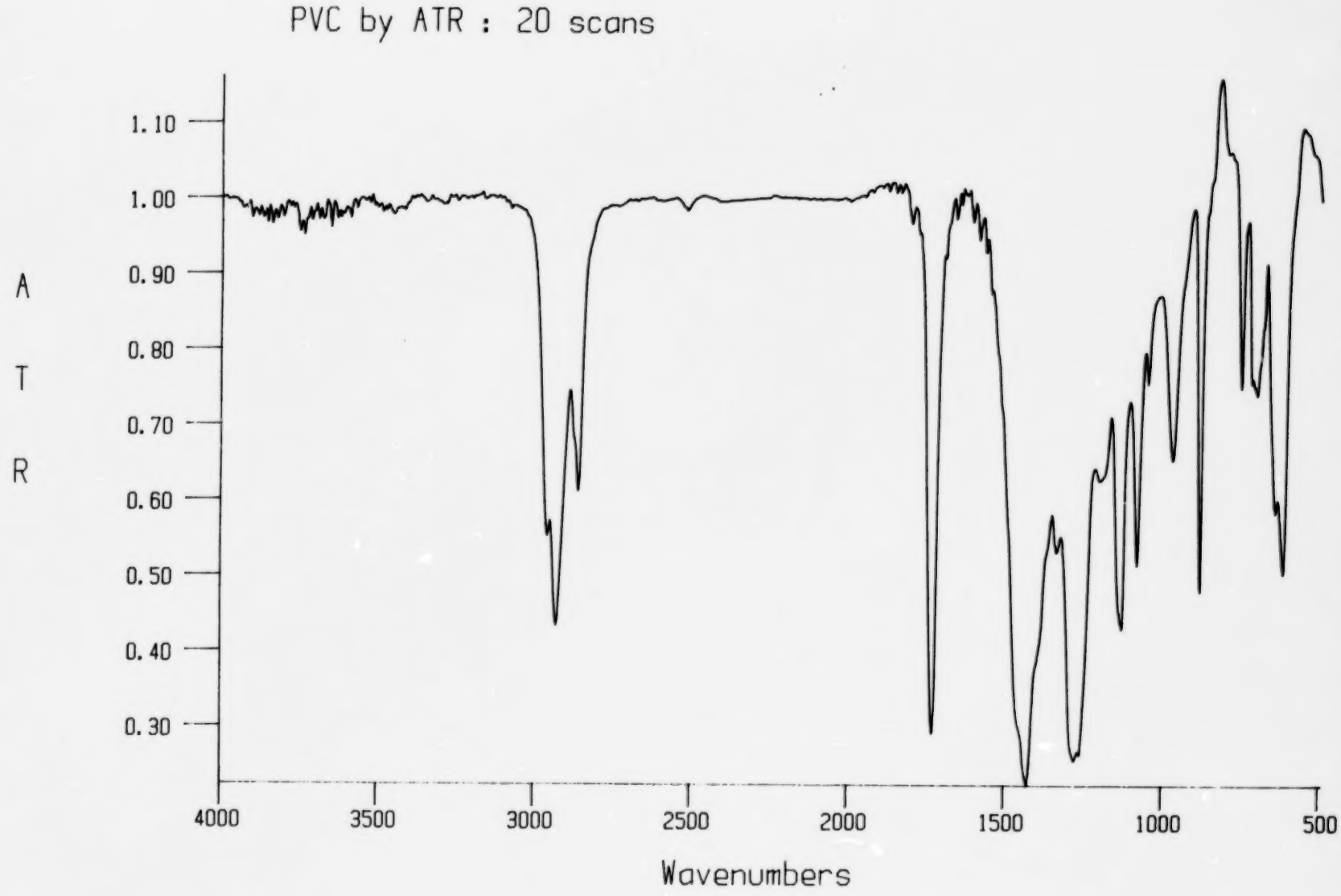

PVC by ATR : 20 scans
A
T
R
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
atrpvcA.ras

FIGURE 10

for highly absorbing liquids which would require very short path-length liquid cells which are expensive and difficult to handle. The short penetration distance can also be of advantage with solid samples for surface measurements. The depth of penetration can be decreased by increasing the angle of incidence and by increasing the refractive index of the sample. A recent paper /6/ shows that under favourable circumstances a spectrum can be obtained from a film of 50 A° thickness on top of an absorbing bulk layer. When the surface layer is representative of the bulk, increased penetration is generally desirable in order to increase signal strength. Improved sensitivity can also be achieved by increasing the number of reflections occurring in the crystal by using a thinner crystal. A spectrum of plasticized polyvinyl chloride (from a waterstop sample) is shown in Figure 10. This spectrum was very easily acquired by placing a thin slice of the sample in contact with a KRS5 (thallium bromoiodide) crystal.

The refractive index of a sample changes with frequency. Dramatic changes can occur at frequencies near a strong absorption band. These changes can be great enough to cause the effective critical angle of the particular sample/crystal combination to become greater than the angle of incidence and thus the condition for internal reflectance is lost. If this occurs, absorbance bands can be severely distorted, resulting in highly asymmetric peaks and apparent baseline drift. This phenomenon is frequently observed in ATR. Increasing the angle of incidence or changing to a crystal of higher refractive index may resolve these problems. These problems and others are discussed in the text by Harrick /7/ which is still the only book devoted to internal reflection spectroscopy. Both theoretical aspects and practical applications of ATR are presented in the Journal of Applied Spectroscopy.

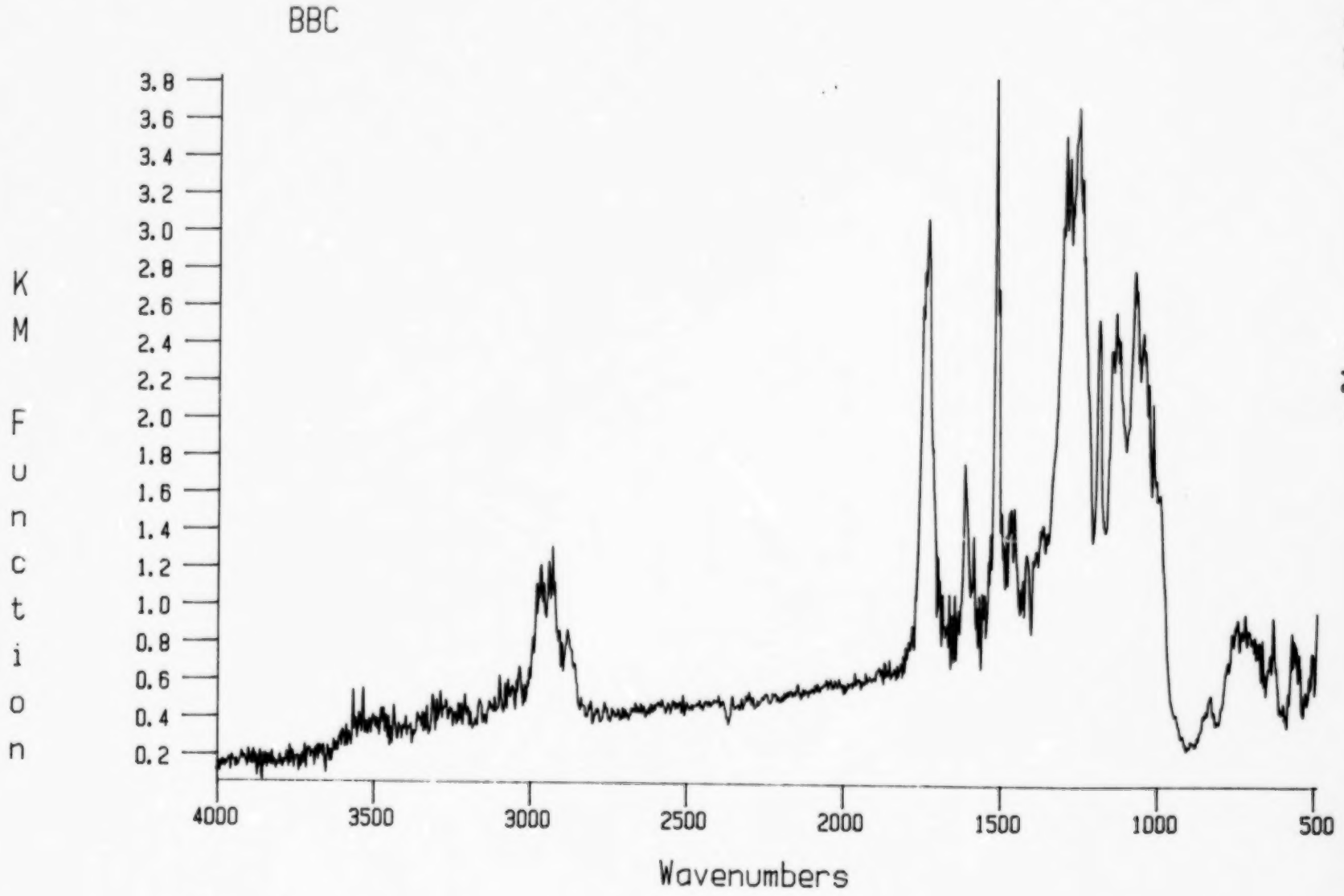
4.4 Diffuse Reflectance

Diffuse reflectance is used with highly scattering samples with rough surfaces such as minerals, powders, papers or liquids which have been dried on powdered KBr. This technique has the lowest S/N of all the methods discussed so far. Although it has been used successfully a number of times with the present configuration (air-cooled source, DTGS detector), it is generally used with a more intense water-cooled source and a liquid nitrogen cooled MCT detector. Specular reflection is often a complicating factor which causes spectral distortions. These can be minimized by reducing the particle size of powders or roughening reflective surfaces. In spite of experimental difficulties, there has been considerable interest in diffuse reflectance methods recently because of the possibility of examining otherwise intractable or difficult samples. A number of papers (for example /8,9/) have dealt with making the method quantitative. Improvements in instrumentation continue to

make the method more convenient /10/ and free from specular distortions /11/. Figure 11 is the spectrum of a highly-filled cured epoxy. Because the sample was insoluble in any solvents (highly cross-linked), very rigid (not suitable for ATR) and had a dull, rough surface, none of the other methods could be used. The only other option was to pyrolyze the sample, but this would be inconvenient and in many cases undesirable because the actual sample spectrum is desired. Although it is possible to grind a portion of the sample, this often exposes a greater portion of the highly absorbing filler and none of the resin spectrum is seen. In this instance, a newly suggested method was used. The surface of the sample was lightly sanded with #320 silicon carbide paper and the spectrum of the paper with embedded resin was obtained by diffuse reflectance (better results are obtained with a fine than a coarse paper). A reference spectrum is obtained by embedding KBr in a similar piece of sandpaper. The silicon carbide paper has essentially no contribution to the spectrum. In addition to the convenience of the method it offers the advantage that the resin tends to be more concentrated relative to the filler at the sample surface thereby enhancing its spectrum.

5.0 COMMENTS AND CONCLUSIONS

The examples above demonstrate that the new instrumentation is capable of obtaining spectra from a variety of samples which were formerly very difficult or impossible to handle by dispersive instrumentation. Additional improvements on the instrumentation are possible which would increase capabilities still further. At this stage we are still learning to make full use of current facilities since these represent a quantum leap over the old dispersive instrumentation. Contrary to some expectations operator involvement is increased. The optimum combination of sample preparation and measurement must be chosen. The operator must be aware of the pitfalls of each technique (including spectral manipulations) which can result in artifacts (false peaks) and spectral distortions. The final spectrum must then be interpreted. When a spectral library is available for the particular sample type and technique used, (a small library of polymer pyrolysates in our case), computer matching can speed up spectral searching considerably and be a great aid, but the operator must evaluate the "matches" found very carefully - the computer will assign the closest matches it can find, no matter how ridiculous. New capabilities bring new responsibilities and the need for additional knowledge and judgment in order to avoid new levels of chaos. The full exploitation of these powerful new techniques will require more time and effort but will yield valuable information in areas of interest to Ontario Hydro such as the behaviour of coatings under adverse conditions,



BBClong.drt

FIGURE 11

the permeability and reactivity of various materials exposed to tritium, etc. - in many cases involving materials which could not formerly be studied because of low S/N.

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